Principles of superconductivity

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The purpose of this chapter is to discuss the main principles of superconductivity as a phenomenon, valid for every superconductor independently of its characteristic properties and material. The underlying mechanisms of superconductivity can be different for various materials, but certain principles must be satisfied. The chapter introduces four principles of superconductivity. (The chapter is slightly modified from the original one in order to be self-contained.)

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The issue of room-temperature superconductivity is the main topic of this book. Even if this subject was raised for the first time before the development of the BCS theory and later by Little in 1964 [1], from the standpoint of practical realization, this issue is still a new, "untouched territory." To go there, we need to know Nature's basic rules for arrangement of matter over there. Otherwise, this journey will face a *fiasco*. To have the microscopic BCS theory in a bag is very useful, but not enough. It is clear to everyone by now that a room-temperature superconductor can not be of the BCS type. Therefore, we need to know more general rules, principles of superconductivity that incorporate also the BCS-type superconductivity as a particular case.

The purpose of this chapter is to discuss the main principles of superconductivity as a phenomenon, valid for every superconductor independently of its characteristic properties and material. The underlying mechanisms of superconductivity can be different for various materials, but certain principles must be satisfied. One should however realize that the principles of superconductivity are not limited to those discussed in this chapter: it is possible that there are others which we do not know yet about.

The first three principles of superconductivity were introduced in [2].

I. FIRST PRINCIPLE OF SUPERCONDUCTIVITY

The microscopic theory of superconductivity for *conventional* superconductors, the BCS theory, is based on Leon Cooper's work published in 1956. This paper was the first major breakthrough for understanding the phenomenon of superconductivity on a *microscopic* scale. Cooper showed that electrons in a solid would always form pairs if an attractive potential was present. It did not matter if this potential was very weak. It is interesting that, during his calculations, Cooper was not looking for pairs—they just "dropped out" of the mathematics. Later it became clear that the interaction of electrons with the lattice allowed them to attract each other despite their mutual Coulomb repulsion. These electron pairs are now known as Cooper pairs.

An important note: in this chapter, we shall use the term "a Cooper pair" more generally than its initial meaning. In the framework of the BCS theory, the Cooper pairs are formed in momentum space, not in real space. Further, we shall consider the case of electron pairing in real space. For simplicity, we shall sometimes call electron pairs formed in real space also as Cooper pairs.

In solids, superconductivity as a quantum state cannot occur without the presence of bosons. Fermions are not suitable for forming a quantum state since they have spin and, therefore, they obey the Pauli exclusion principle according to which two identical fermions cannot occupy the same quantum state. Electrons are fermions with a spin of 1/2, while Cooper pairs are already composite bosons since the value of their total spin is either 0 or 1. Therefore, the electron pairing is an inseparable part of the phenomenon of superconductivity and, in any material, superconductivity cannot occur without electron pairing.

In some unconventional superconductors, the charge carriers are not electrons but holes with a charge of $+|e|$ and spin of 1/2. The reasoning used above for electrons is valid for holes as well. Thus, in the general case, it is better to use the term "quasiparticles" which also reflects the fact that the electrons and holes are in a medium.

The first principle of superconductivity:

Principle 1: **Superconductivity requires quasiparticle pairing**

In paying tribute to Cooper, the first principle of superconductivity can be called the *Cooper principle*.

In the framework of the BCS theory, the quasiparticle (electron) pairing occurs in momentum space, not in real space. Indeed in the next section, we shall see that the electron pairing in conventional superconductors cannot occur in real space because the onset of long-range

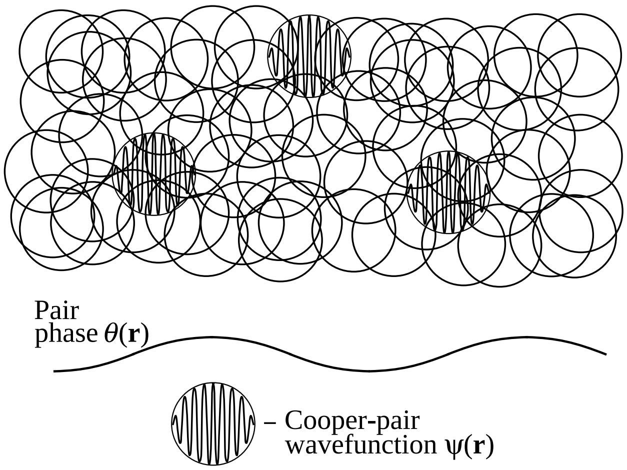

FIG. 1. In conventional superconductors, the superconducting ground state is composed by a very large number of overlapping Cooper-pair wavefunctions, $\psi(\mathbf{r})$. To avoid confusion, only three Cooper-pair wavefunctions are shown in the sketch; the other are depicted by open circles. The phases of the wavefunctions are locked together since this minimizes the free energy. The Cooper-pair phase $\Theta(\mathbf{r})$, illustrated in the sketch, is also the phase of the order parameter $\Psi(\mathbf{r})$.

phase coherence in classical superconductors occurs due to the overlap of Cooper-pair wavefunctions, as shown in Fig. 1. As a consequence, the order parameter and the Cooper-pair wavefunctions in conventional superconductors are the same: the order parameter is a "magnified" version of the Cooper-pair wavefunctions. However, in unconventional superconductors, the electron pairing is not restricted by the momentum space because the order parameter in unconventional superconductors has nothing to do with the Cooper-pair wavefunctions. *Generally speaking*, the electron pairing in unconventional superconductors may take place not only in momentum space but also in real space. We shall discuss such a possibility in the following section.

The electron pairing in momentum space can be considered as a *collective* phenomenon, while that in real space as *individual*. We already know that the density of free (conduction) electrons in conventional superconductors is relatively high ($\sim 5 \times 10^{22}$ cm^{-3}); however, only a small fraction of them participate in electron pairing ($\sim 0.01\%$). In unconventional superconductors it is just the other way round: the electron density is low ($\sim 5 \times 10^{21}$ cm^{-3}) but a relatively large part of them participate in the electron pairing ($\sim 10\%$). Independently of the space where they are paired—momentum or real—two electrons can form a bound state **only if** *the net force acting between them is attractive*.

II. SECOND PRINCIPLE OF SUPERCONDUCTIVITY

After the development of the BCS theory in 1957, the issue of long-range phase coherence in superconductors was not discussed widely in the literature because, in conventional superconductors, the pairing and the onset of phase coherence take place simultaneously at T_c. The onset of phase coherence in conventional superconductors occurs due to the overlap of Cooper-pair wavefunctions, as shown in Fig. 1. Only after 1986 when high-T_c superconductors were discovered, the question of electron pairing above T_c appeared. So, it was then realized that it is necessary to consider the two processes—the electron pairing and the onset of phase coherence—separately and independently of one another [3].

In many unconventional superconductors, quasiparticles become paired above T_c and start forming the superconducting condensate only at T_c. Superconductivity requires both the electron pairing and the Cooper-pair condensation. Thus, the second principle of superconductivity deals with the Cooper-pair condensation taking place at T_c. This process is also known as the onset of long-range phase coherence.

Principle 2: **The transitioninto the superconducting state is the Bose-Einstein-like condensation and occurs in momentum space**

Let us first start with one main difference between fermions and bosons. Figure 2 schematically shows an ensemble of fermions and an ensemble of bosons at $T \gg 0$ and $T = 0$. In Fig. 2 one can see that, at high temperatures, both types of particles behave in a similar manner by distributing themselves in their energy levels somewhat haphazardly but with more of them toward lower energies. At absolute zero, the two types of particles rearrange themselves in their lowest energy configuration. Fermions obey the Pauli exclusion principle. Therefore, at absolute zero, each level from the bottom up to the Fermi energy E_F is occupied by two electrons, one with spin up and the other with spin down, as shown in Fig. 2. At absolute zero, all energy levels above the Fermi level are empty. In contrast to this, bosons do not conform to the exclusion principle, therefore, at absolute zero, they all consolidate in their lowest energy state, as shown in Fig. 2. Since all the bosons are in the same quantum state, they form a quantum condensate (which is similar to a superconducting condensate). In practice, however, absolute zero is not accessible.

We are now ready to discuss the so-called *Bose-Einstein condensation*. In the 1920s, Einstein predicted that if an ideal gas of identical atoms, i.e. bosons, at thermal equilibrium is trapped in a box, at sufficiently

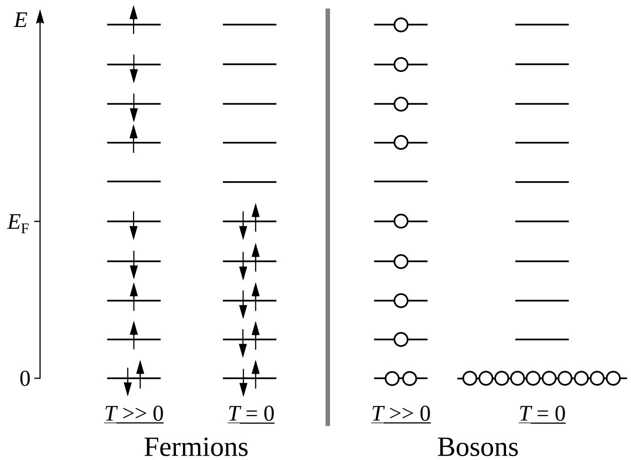

FIG. 2. Sketch of the occupation of energy levels for fermions and bosons at high temperatures and absolute zero. Arrows indicate the spin direction of the fermions. For simplicity, the spin of the bosons is chosen to be zero. E_F is the Fermi level for the fermions.

low temperatures the particles can in principle accumulate in the lowest energy level (see Fig. 2). This may take place only if the quantum wave packets of the particles overlap. In other words, the wavelengths of the matter waves associated with the particles—the *Broglie waves*—become similar in size to the mean particle distances in the box. If this happens, the particles condense, almost motionless, into the lowest quantum state, forming a Bose-Einstein condensate. So, the Bose-Einstein condensation is a macroscopic quantum phenomenon and, thus, similar to the superconducting condensation.

For many decades physicists dreamt of cooling a sufficiently large number of ordinary atoms to low enough temperatures to undergo the Bose-Einstein condensation spontaneously. During 1995 this was accomplished by three groups acting independently. The first Bose-Einstein condensate was formed by using rubidium atoms cooled to 2×10^{-9} K.

The superconducting and Bose-Einstein condensates have much in common but also a number of differences. Let us start with their similarities. Firstly, the superconducting and Bose-Einstein condensations are both quantum phenomena occurring on a macroscopic scale. Thus, every Bose-Einstein condensate exhibits most of the superconducting-state properties. Secondly, the superconducting and Bose-Einstein condensations both occur in momentum space, not in real space. What is the difference between a condensation in momentum space and one in real space? For example, the vapor-liquid transition is a condensation in ordinary space. After the transition, the average distance between particles (atoms or molecules) is changed—becomes smaller when the vapor condenses and larger when the liquid evaporates. So, if a condensation takes place in real space, there may be some noticeable changes in the system (second-order phase transitions occurring in real space, if such exist, are not accompanied by changes in real space). On the other hand, if a condensation occurs in momentum space there are no changes in ordinary space. In the aforementioned example of the Bose-Einstein condensation occurring in the box, after the condensation, the mean distance between particles remains the same.

The superconducting and Bose-Einstein condensates have two major differences. In spite of the fact that the superconducting and Bose-Einstein condensates are both quantum states, they, however, have "different goals to achieve." Through the Bose-Einstein condensation bosons assume to reach the lowest energy level existing in the system (see Fig. 2). At the same time, the Cooper pairs try to descend below the Fermi level as deeply as possible, generating an energy gap. The second difference is that a Bose-Einstein condensate consists of real bosons, while a superconducting condensate comprises composite bosons. To summarize, the two condensates—superconducting and Bose-Einstein—have common quantum properties, but also, they have a few differences.

In conventional superconductors, the onset of phase coherence occurs due to the overlap of Cooper-pair wavefunctions. In a sense, it is a passive process because the overlap of wavefunctions does not generate an order parameter—it only makes the Cooper-pair wavefunctions be in phase. This means that in order to form a superconducting condensate, the Cooper pairs in conventional superconductors must be paired in momentum space, not in ordinary space. However, this may not be the case for unconventional superconductors where the onset of long-range phase coherence occurs due to not the overlap of Cooper-pair wavefunctions but due to another "active" process. As a consequence, if the onset of phase coherence in unconventional superconductors takes place in momentum space, it relieves the Cooper pairs of the duty to be paired in momentum space. This means that, in unconventional superconductors, the Cooper pairs may be formed in real space. Of course, they are not required to, but they may.

If the Cooper pairs in some unconventional superconductors are indeed formed in real space, this signifies that the BCS theory and the future theory for unconventional superconductors can hardly be unified.

Let us go back to the second principle of superconductivity. After all these explanations, the meaning of this principle should be clear. The transition into the superconducting state always occurs in momentum space, and this condensation is similar to that predicted by Einstein.

III. THIRD PRINCIPLE OF SUPERCONDUCTIVITY

If the first two principles of superconductivity, in fact, are just the ascertaining of facts and can hardly be used for future predictions, the third and fourth principles are better suited for this purpose.

The third principle of superconductivity is:

Principle 3: **The mechanism of electron pairing and the mechanism of Cooper-pair condensation must be different**

The validity of the third principle of superconductivity will be evident after the presentation of the fourth principle. Historically, this principle was introduced first [2].

It is worth to recall that, in conventional superconductors, phonons mediate the electron pairing, while the overlap of wavefunctions ensures the Cooper-pair condensation. In the unconventional superconductors from the third group of superconductors, such as the cuprates, organic salts, heavy fermions, doped C_{60} etc., phonons also mediate the electron pairing, while spin fluctuations are responsible for the Cooper-pair condensation. So, in all superconductors, the mechanism of electron pairing differs from the mechanism of Cooper-pair condensation (onset of long-range phase coherence). Generally speaking, if in a superconductor, the same "mediator" (for example, phonons) is responsible for the electron pairing and for the onset of long-range phase coherence (Cooper-pair condensation), this will simply lead to the collapse of superconductivity (see the following section).

Since in solids, phonons and spin fluctuations have two channels—acoustic and optical—*theoretically*, it is possible that one channel can be responsible for the electron pairing and the other for the Cooper-pair condensation. The main problem, however, is that these two channels—acoustic and optical—usually compete with one another. So, it is very unlikely that such a "cooperation" will lead to superconductivity.

IV. FOURTH PRINCIPLE OF SUPERCONDUCTIVITY

If the first three principles of superconductivity do not deal with numbers, the forth principle can be used for making various estimations.

Generally speaking, a superconductor is characterized by a pairing energy gap Δ_p and a phase-coherence gap Δ_c. For genuine (not proximity-induced) superconductivity, the phase-coherence gap is proportional to T_c:

$$2\Delta_c = \Lambda\, k_B T_c, \tag{1}$$

where Λ is the coefficient proportionality [not to be confused with the phenomenological parameter Λ in the London equations]. At the same time, the pairing energy gap is proportional to the pairing temperature T_{pair}:

$$2\Delta_p = \Lambda'\, k_B T_{pair}. \tag{2}$$

Since the formation of Cooper pairs must precede the onset of long-range phase coherence, then in the general case, $T_{pair} \geq T_c$.

In conventional superconductors, however, there is only one energy gap Δ which is in fact a pairing gap but proportional to T_c:

$$2\Delta = \Lambda\, k_B T_c, \tag{3}$$

This is because, in conventional superconductors, the electron pairing and the onset of long-range phase coherence take place at the same temperature—at T_c. In all known cases, the coefficients Λ and Λ' lie in the interval between 3.2 and 6 (in one heavy fermion, ~ 9). Thus, we are now in position to discuss the fourth principle of superconductivity:

Principle 4: **For genuine, homogeneous superconductivity, $\Delta_p > \Delta_c > \frac{3}{4}k_B T_c$ always (in conventional superconductors, $\Delta > \frac{3}{4}k_B T_c$)**

Let us start with the case of conventional superconductors. The reason why superconductivity occurs exclusively at low temperatures is the presence of substantial thermal fluctuations at high temperatures. The thermal energy is $\frac{3}{2}k_B T$. In conventional superconductors, the energy of electron binding, 2Δ, must be larger than the thermal energy; otherwise, the pairs will be broken up by thermal fluctuations. So, the energy 2Δ must exceed the energy $\frac{3}{2}k_B T_c$. In the framework of the BCS theory, the ratio between these two energies, $2\Delta/(k_B T_c) \simeq 3.52$, is well above 1.5.

In the case of unconventional superconductors, the same reasoning is also applicable for the phase-coherence energy gap: $2\Delta_c > \frac{3}{2}k_B T_c$.

We now discuss the last inequality, namely, $\Delta_p > \Delta_c$. In unconventional superconductors, the Cooper pairs condense at T_c due to their interaction with some bosonic excitations present in the system, for example, spin fluctuations. These bosonic excitations are directly coupled to the Cooper pairs, and the strength of this coupling with each Cooper pair is measured by the energy $2\Delta_c$. If the strength of this coupling will exceed the pairing energy $2\Delta_p$, the Cooper pairs will immediately be broken up. Therefore, the inequality $\Delta_p > \Delta_c$ must be valid.

What will happen with a superconductor if, at some temperature, $\Delta_p = \Delta_c$? Such a situation can take place either at T_c, defined *formally* by Eq. (1), or below T_c,

i.e. inside the superconducting state. In both cases, the temperature at which such a situation occurs is a critical point, T_{cp}. If the temperature remains constant, locally there will be superconducting fluctuations due to thermal fluctuations, thus, a kind of inhomogeneous superconductivity. If the temperature falls, two outcomes are possible (as it usually takes place at a critical point). In the first scenario, superconductivity will never appear if $T_{cp} = T_c$, or will disappear at T_{cp} if $T_{cp} < T_c$. In the second possible outcome, homogeneous superconductivity may appear. The final result depends completely on bosonic excitations that mediate the electron pairing and that responsible for the onset of phase coherence. The interactions of these excitations with electrons and Cooper pairs, respectively, vary with temperature. If, somewhat below T_{cp}, the strength of the pairing binding increases *or/and* the strength of the phase-coherence adherence decreases, homogeneous superconductivity will appear. In the opposite case, superconductivity will never appear, or disappear at T_{cp}. It is worth noting that, in principle, superconductivity may reappear at $T < T_{cp}$.

The cases of disappearance of superconductivity below T_c are well known. However, it is assumed that the cause of such a disappearance is the emergence of a ferromagnetic order. As well known, the Chevrel phase $HoMo_6S_8$ is superconducting only between 2 and 0.65 K. The erbium rhodium boride $ErRh_4B_4$ superconducts only between 8.7 and 0.8 K. The cuprate Bi2212 doped by Fe atoms was seen superconducting only between 32 and 31.5 K [4]. The so-called $\frac{1}{8}$ anomaly in the cuprate LSCO, discussed in Chapter 3, is caused apparently by *static* magnetic order [2] which may result in the appearance of a critical point where $\Delta_p \simeq \Delta_c$.

It is necessary to mention that the case $\Delta_p = \Delta_c$ must not be confused with the case $T_{pair} = T_c$. There are unconventional superconductors in which the electron pairing and the onset of phase coherence occur at the same temperature, i.e. $T_{pair} \simeq T_c$. This, however, does not mean that $\Delta_p = \Delta_c$ because $\Lambda \neq \Lambda'$ in Eqs. (1) and (2). Usually, $\Lambda' > \Lambda$. For example, in hole-doped cuprates, $2\Delta_p/k_BT_{pair} \simeq 6$ and, depending on the cuprate, $2\Delta_c/k_BT_c = 5.2$–5.9.

Finally, let us go back to the third principle of superconductivity to show its validity. The case in which the same bosonic excitations mediate the electron pairing **and** the phase coherence is equivalent to the case $\Delta_p = \Delta_c$ discussed above. Since, in this particular case, the equality $\Delta_p = \Delta_c$ is independent of temperature, the occurrence of homogeneous superconductivity is impossible.

V. PROXIMITY-INDUCED SUPERCONDUCTIVITY

The principles considered above are derived for genuine superconductivity. By using the same reasoning as that in the previous section for proximity-induced superconductivity, one can obtain a useful result, namely, that $2\Delta \sim \frac{3}{2}k_BT_c$, meaning that the energy gap of proximity-induced superconductivity should be somewhat larger than the thermal energy. Of course, to observe this gap for example in tunneling measurements may be not possible if the density of induced pairs is low. This case is reminiscent of gapless superconductivity [5]. Hence, we may argue that

For proximity-induced superconductivity, at low temperature, $2\Delta_p \geq \frac{3}{2}k_BT_c$

One should however realize that this is a general statement; the final result depends also upon the material and, in the case of thin films, on the thickness of the normal layer.

What is the maximum critical temperature of BCS-type superconductivity? In conventional superconductors, $\Lambda = 3.2$–4.2 in Eq. (3). Among conventional superconductors, Nb has the maximum energy gap, $\Delta \simeq 1.5$ meV. Then, taking $\Delta^{BCS}_{max} \approx 2$ meV and using $\Lambda = 3.2$, we have $T^{BCS}_{c,max} = 2\Delta^{BCS}_{max}/3.2k_B \approx 15$ K for conventional superconductors. Let us now estimate the maximum critical temperature for induced superconductivity of the BCS type in a material with a strong electron-phonon interaction. In such materials, genuine superconductivity (if exists) is in the strong coupling regime and characterized by $\Lambda \simeq 4.2$ in Eq. (3). Assuming that the same strong coupling regime is also applied to the induced superconductivity with $2\Delta \sim 1.5k_BT^{ind}_c$ and that, in the superconductor which induces the Cooper pairs, $\Delta_p \gg 2$ meV, one can then obtain that $T^{ind}_{c,max} \sim 15$ K $\times \frac{4.2}{1.5} \simeq 42$ K.

If the superconductor which induces the Cooper pairs is of the BCS type, the value $\Delta^{ind}_{max} = 2$ meV can be used to estimate $T^{ind}_{c,max}$ independently. Substituting the value of 2 meV into $2\Delta \sim 1.5k_BT^{ind}_c$, we have $T^{ind}_{c,max} \simeq 31$ K which is lower than 42 K.

In second-group superconductors which are characterized by the presence of two superconducting subsystems, the critical temperature never exceeds 42 K. For example, in MgB_2, $T_c = 39$ K and, for the smaller energy gap, $2\Delta_s \simeq 1.7k_BT_c$ [2]. At the same time, for the larger energy gap in MgB_2, $2\Delta_L \simeq 4.5k_BT_c$ or $\Delta_L \simeq 7.5$ meV. Then, on the basis of the estimation for $T^{ind}_{c,max}$, it is more or less obvious that, in MgB_2, one subsystem with genuine superconductivity (which is low-dimensional), having $\Delta_L \simeq 7.5$ meV, induces superconductivity into another subsystem and the latter one controls the bulk T_c.

The charge carriers in compounds of the first and second groups of superconductors are electrons. Is there hole-induced superconductivity? Yes. At least one case of hole-induced superconductivity is known: in the cuprate YBCO, the CuO chains become superconducting due to the proximity effect. The value of the superconducting energy gap on the chains in YBCO is well documented; in optimally doped YBCO, it is about 6 meV [2]. Using $T_{c,max} = 93$ K for YBCO and $\Delta \sim 6$ meV, one obtains $2\Delta/k_B T_c \simeq 1.5$. This result may indicate that the bulk T_c in YBCO is controlled by induced superconductivity on the CuO chains.

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